Thermoluminescence dating of sediments using mineral zircon

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2. THERMOLUMINESCENCE THEORY

2.1 Introduction

The phenomenon of thermoluminescence (TL) of minerals was known empirically as early as 1663. It was in this year that Sir Robert Boyle reported to the Royal Society about ***"Experiments and Considerations upon Colours with Observations on Diamond That Shines in the Dark"*** (1663) and described how, upon warming a diamond in contact with his body in the dark, he saw a flash. This reflects the definition of thermoluminescence. Not only diamonds but a large number of minerals emit light energy upon warming. Well-known examples are quartz, feldspar, calcite and flint. But the phenomenon of thermoluminescence itself was not sufficient to be used as a dating method. It was necessary to establish the mechanisms, which are responsible for resetting the dating clock and link the intensity of the emitted light energy to a time scale. Three centuries later the *first law* of thermoluminescence was established, which states that the thermoluminescence of minerals is roughly proportional to the irradiation dose to which they had been exposed (Roth et al, 1989).

Another important observation for making TL a useful tool for dating was that, if the same mineral is re-heated, no more light is emitted, and it is only after the application of a new radiation dose that light may again be emitted.

2.2 Basic mechanism

Thermoluminescence is the thermally stimulated emission of light from an insulator or a semiconductor following the previous absorption of energy from ionizing radiation. The thermoluminescence process can be understood in terms of the band structure model of insulators.

In a pure insulator there are two relevant energy bands: (i) an almost completely filled valence band and (ii) an almost empty conduction band. The two energy bands are separated by a forbidden gap, which means that between these two bands there are no electronic energy levels. Transitions of electrons between the valence band and the conduction band are allowed and they produce “free” electrons in the conduction band and “free” holes in the valence band. The energy difference between the two bands is denoted by the band-gap energy E_g (figure 2.1).

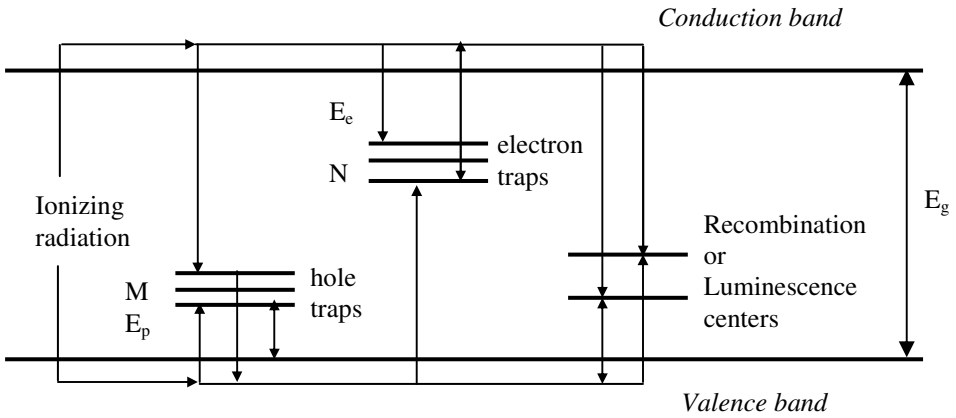

Figure 2.1. *Energy-level presentation of the thermoluminescence process, showing the filling process of the electron and hole traps and the mechanism, which is responsible for thermally activated luminescence (TL). N= the total concentration of electron traps with energy E_e, M=the total concentration of hole traps with energy E_p.*

Imperfections in the crystal, associated with impurities and/or lattice defects may create new localized energy levels in the forbidden band gap. The positions of the energy levels depend on the nature of the imperfections/defects and the host lattice. Some of these defects are capable to trap an electron or a hole. Therefore the centers are referred to as electron or hole traps and after trapping an electron or hole the new defects are called trapped electron or trapped hole centers, respectively. The most simple trapped electron center is the F-center, which is an anion vacancy in the crystal lattice after it has trapped an electron. The name 'F-center' is derived from the German word 'Farbe', which means color. When the concentration of F-centers is sufficient, the crystal absorbs sufficient light in a limited frequency range and as a result, the crystal is colored. To maintain electroneutrality of the crystal, for each electron, which is trapped at an electron trap a hole is produced, which might be trapped at a hole trap. After trapping a trapped hole is formed.

The F-center in NaCl can be regarded as the proto-type of the trapped electron centers, which has been studied in great detail since the 1930's. The energy levels of the well-known F-center in NaCl, which is an electron trapped at a vacant anion position in the NaCl crystal lattice (figure 2.2), are located a few eV below the bottom of the conduction band. Between the energy levels transitions can be induced by absorption of light, which can be characterized as 1s-2p transitions and give rise to the so-called F-band. The electronic F-center wave functions are confined to a volume corresponding to a few molecules.

Another class of imperfections is associated with impurities, e.g. transition ions, which are quite often the reason why certain minerals show a characteristic color. The color is due to absorption bands caused by electronic transitions between energy levels in the band gap. The wave functions of the transition ions (in particular 4f-ions) are highly localized. The

energy levels in the band gap depend, as mentioned above, on the nature of the imperfection, lattice defect or impurity and can in principle be located at any energy position varying from just below the bottom of the conduction band to just above the top of the valence band.

Optical transitions between energy levels located in the forbidden band gap may occur if they are allowed according to existing selection rules, which depend on the symmetry properties of the ground and excited state, but also transitions between the energy levels in the gap and empty more or less localized electronic levels in the conduction band are possible. Obviously, the latter transition results in empty electron traps in the band gap. Eventually, the electrons may escape from the centers associated with these energy levels and could return later at these locations by re-trapping. This description leads us to the definition of electron traps, which are localized defects in the crystal where electrons (conduction electrons or electrons from other centers) can be trapped. Accordingly, these centers can be filled or empty. This general description can be applied as an example to very simple centers, like the F-center in alkali halides. In this most simple example, the filled trap corresponds with the F-center, while the empty trap is an anion vacancy.

An analogous discussion can be given for hole-type centers. As mentioned above the valence band is filled almost completely, which implies that free holes exist in this band. Similar to the description for electronic levels in the band gap and the trapping and de-trapping processes it is possible to consider centers with energy levels in the forbidden band gap, which are capable of trapping free holes, which are available in the valence band. Like the trapped electrons, trapped holes can be released thermally or optically. After releasing the trapped hole a hole trap is left.

A variety of defects belonging to the above-mentioned two classes of centers, which are associated with energy levels in the forbidden band gap, are also produced during exposure to ionizing radiation. Well-known examples of radiation-induced defect centers are the F-center (the proto-type electron center, which has been described above) and a variety of V-centers. V-centers form a group of defects, which absorb light in the violet part of the optical spectrum. This property is the reason why these centers are called V-centers. An important property of V-centers is that they have trapped a hole, which is produced simultaneously with the electron. The most simple V-center is the V_k-center in alkali halides, which is referred to as a “self-trapped hole”. It consists of a hole trapped at two neighboring chloride ions at regular lattice positions in the NaCl crystal (figure 2.2). The hole therefore belongs predominantly to two neighboring Cl^--ions. After the hole is trapped, the chloride ions of the resulting Cl_2^- molecule are displaced considerably from their original lattice positions (figure 2.2). This implies that the V_k-center is in fact a Cl_2^- center.

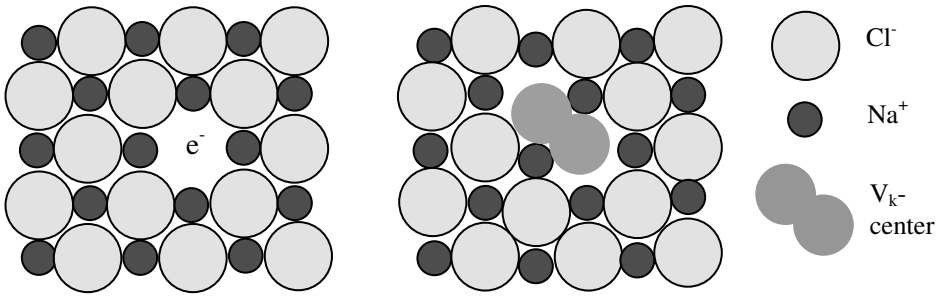

Figure 2.2. *Two dimensional representation of a NaCl crystal showing the F-center (a), and the V_k-center (b) in NaCl. The F-center is the proto-type of trapped electron centers and the V_k center is the most simple trapped hole center.*

Due to ionizing radiation electrons are transferred from the valence band to the conduction band, which leads to the presence of significant concentrations of free electrons (in the conduction band) and free holes (in the valence band). In ionic materials, quite often the primary radiolytic reactions resulting from interactions between radiation and the crystal take place at anions (e.g. the Cl^- or O^{2-} ions in case of chlorides or oxides, respectively). Due to these processes excitations with binding energies slightly smaller than the forbidden band gap take place. These excitations are called excitons. Usually, the subsequent de-excitation processes are sufficiently energetic and effective to induce atomic/ionic displacements in the crystal lattice, which leads to the formation of radiation damage, i.e. radiation induced defects.

From the point of view of TL dating, exposure to ionizing radiation has two important consequences:

I radiation induced defects (both electron and hole traps) are created and;

II free electrons and holes are created in the conduction band and the valence band, respectively.

As long as the concentration of radiation-induced defects is small, the number of defects usually increases with increasing radiation dose. Ultimately, for very high doses, one might expect that the concentration of the radiation-induced defects saturates. I.e., with increasing dose the concentration of radiation-induced defects reaches a maximum value. In zircon the radiation damage may reach very high levels. Due to their long-term exposure to ionizing radiation extremely old minerals are often *metamict*, which means that the long-range order is absent and the structural properties of these minerals are similar to those of amorphous materials like glasses. These heavily damaged minerals are not suited for TL dating purposes. As a result of the structural changes during the long-term exposure, the physical properties, in particular the TL controlling properties, have changed drastically. In addition, very old zircons are usually not transparent; i.e. they absorb the TL quanta, which affects the dating results.

The continuous production of free electrons and holes as a result of the exposure to ionizing radiation is essential for the production of sufficiently stable defects, which produce TL. Due to the high mobility, free electrons and holes can migrate in the crystal until they are trapped by impurities, luminescent centers and other imperfections in the crystal. During irradiation the electrons and holes are (re-)distributed continuously over the available electron and hole traps. A necessary condition for a mineral to be a suitable luminescent material for TL dating is that the relevant traps are deep, i.e. not easily emptied. This implies that the energy of the trapped electron should be located sufficiently far from the bottom of the conduction band. Similarly, the energy of the trapped hole should be located sufficiently far from the top of the valence band.

A trap is characterized by the energy E that a trapped electron (or hole) must acquire from lattice vibrations to escape to the conduction band (or valence band). Electrons in the conduction band can move freely in the crystal. Holes, which were removed from hole traps are free to move in the crystal, when they are excited to energy levels in the valence band. There is a characteristic temperature at which the thermal vibrations of the crystal lattice are sufficient to cause the release of trapped electrons. Some of the released electrons reach luminescence centers, which are filled with holes, and light is emitted in the recombination process. A similar reasoning holds for the case of luminescence produced by recombination of free holes at the electronic recombination centers. Figure 2.1 shows the schematic representation of the thermoluminescence process in an insulating crystal with forbidden gap width E_g. In the following, only hole-type luminescence centers will be considered because we will show that in zircon the important TL activators consist of trapped holes.

2.3 Rate equations

The processes, which have been schematically described above, can be summarized as follows with a simplified model (figure 2.1). The trapped electron is liberated from the trap by heating the crystal to moderate temperatures; it crosses a certain potential-energy barrier and when the electron recombines with a hole trapped at a recombination center, both defect centers annihilate. This recombination process is sometimes accompanied by emission of light. The rate at which the electrons, or holes, escape from the traps is roughly governed by the vibrational frequency (or attempt-to-escape factor) s of the charge within the trap and the height E of the potential energy barrier, which is referred to as the trap depth. The overall escape rate is proportional to $s \cdot exp(-E/k_BT)$ The remaining parameters in the formula are k_B, which is the Boltzmann factor and T is the absolute temperature. By heating a crystal with trapped electrons the luminescence signal starts at zero intensity (no electrons escaping), increases with increasing temperature (according to the above mentioned Boltzmann factor) and finally drops to zero at high temperatures when all traps are empty and all luminescence centers have been annihilated. The luminescence phenomenon results in a so-called glow peak (figure 2.3). A detailed analysis of the shape of the glow curve provides information about the trap depth E, frequency factor s, numbers and type of electron and hole traps, the electron mobility and the capture cross sections of the centers, involved in the TL processes.

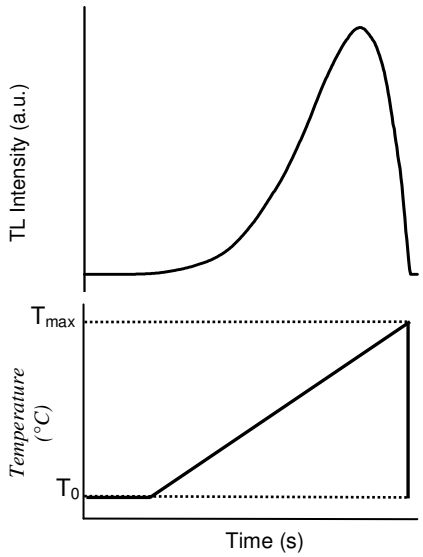

Figure 2.3. *Schematic presentation of the temperature dependence of the luminescence output.*

The kinetics describing the thermoluminescence process was first proposed by Randall and Wilkins, and was based on a simple band model similar to but simpler than the one shown in figure 2.1 (Randall and Wilkins, 1945). They ascribe the occurrence of the TL peak to the thermal release of electrons from traps and their subsequent recombination with holes trapped at recombination centers. In this simple model only one kind of trap (electron traps) and one kind of recombination center (trapped hole centers) is considered, along with mobile electrons. Another assumption is that no direct recombination takes place from the electron trap to the recombination center; electronic transport takes place only via the conduction band. All concentrations to be used below are dimensionless and defined per lattice site

Let us consider an insulating sample with electron and hole traps, which can be described schematically by the band-structure picture presented in figure 2.1. The behavior of the system can be described by a set of differential equations. There is a total concentration of N electron traps with trap depths E_e and a total concentration of M hole traps with trap depth E_p. The concentration of traps, which are occupied by electrons, is denoted by n and the concentration of traps, which are occupied by holes, is denoted by m. During heating the crystal, electrons are released from the traps, producing a concentration n_c of free electrons in the conduction band, and there will be n filled and $(N - n)$ empty traps. The number of electronic excitations per second in which the electrons are transferred to the conduction band obeys Arrhenius' law. According to this law, the number of excitations per second is proportional to the number of electrons n and the Boltzmann factor, $exp(-E_e/k_BT)$,

where E_e is the activation energy or trap depth, k_B is the Boltzmann constant and T the (absolute) temperature.

The electrons, which are excited to the conduction band, depopulate the traps. The corresponding rate equation can be written as

$$\frac{dn}{dt} = -v(T)\,n. \tag{2.1}$$

Here $v(T) = s\exp\left(-E_e/k_BT\right)$ and s is called the frequency factor for trapped electrons. This quantity is called the attempt frequency and depends on the vibration frequency of the ions adjacent to the electron trap. E_e and s are assumed to be temperature independent.

The depopulation of the traps is partly compensated by re-trapping of electrons from the conduction band by the empty traps. The rate of re-trapping is proportional to (i) the concentration of free electrons n_c in the conduction band, (ii) the number of empty traps, which is equal to the total number of traps minus the number of filled traps ($N - n$), and (iii) the factor A_N that characterizes the probability that an electron will be re-trapped. The first important rate equation for TL takes into account both un-trapping processes (2.1) and re-trapping. Thus

$$\frac{dn}{dt} = -v(T)\,n + A_N n_c (N-n)\,. \tag{2.2}$$

Electrons, which have escaped from the traps to the conduction band, have a certain probability to recombine with a hole in a luminescence center, yielding a photon with energy hv, which is characteristic for that particular luminescence center. The rate of recombination is proportional to the number of free (conduction) electrons n_c, the concentration of the filled hole traps m and the probability A_m that an electron will recombine with the hole trapped in the above mentioned type of recombination center. Thus the rate of change of the concentration of free electrons in the conduction band in the recombination process is

$$\left.\frac{dn_c}{dt}\right|_{recombination} = -A_m n_c m\,. \tag{2.3}$$

The rate of change of the number of occupied electron traps, given in (2.2) leads to an equal, but opposite contribution to the rate of change of the number of conduction electrons. Together with the contribution associated with recombination as given in (2.3), we obtain the important rate equation for TL describing the concentration of free electrons exited in the conduction band

$$\frac{dn_c}{dt} = v(T)\,n - A_N\,n_c\,(N-n) - A_m\,n_c\,m\,. \tag{2.4}$$

$v(T)$ has been defined in (2.1).

The lifetime of the electrons in the conduction band is assumed to be very short compared to the characteristic time associated with the release and trapping of the electrons. Hence, the concentrations of the electrons in the conduction band n_c will be small compared with the concentrations of the electrons in the traps n. The electron concentration in the conduction band will adjust very quickly to the variations of the concentrations of filled electron and hole traps. Therefore, the rate of change of the carrier concentrations n_c in the conduction band is very small and it can be approximated to zero: $dn_c/dt = 0$. Therefore (2.4) may be written as

$$\frac{dn_c}{dt} = 0 \quad \Rightarrow \quad v(T)\, n - A_N\, n_c\, (N-n) - A_m\, n_c\, m = 0\,, \tag{2.5}$$

which yields the solution:

$$n_c = \frac{v(T) n}{A_N (N-n) + A_m m}\,. \tag{2.6}$$

When as a result of each recombination event a quantum of light is emitted, the intensity I of the emitted light is equal to the recombination rate of free electrons with trapped holes (the last term on the right-hand side of (2.4))

$$I = A_m n_c m = A_m v(T) \frac{n\, m}{A_N (N-n) + A_m m}\,. \tag{2.7}$$

This is the expression for the luminescence intensity obtained from the general Randall-Wilkins model.

Randall and Wilkins made the assumption that there is a strong tendency to recombination and that electrons, which are released thermally from the traps and excited into the conduction band recombine quickly with trapped holes; i.e. no re-trapping or trapping by any other trap or recombination center is allowed. The assumption that $A_m m >> A_N(N\text{-}n)$ leads to *first-order kinetics thermoluminescence* behavior, which is described by

$$I \approx \frac{A_m v(T) n\, m}{A_m m} = n\, v(T) = s \exp\left(\frac{-E}{k_B T}\right) n\,. \tag{2.8}$$

Second-order kinetics is obtained with the assumption made by Garlick and Gibson, 1948. In this approximation re-trapping dominates. This means that electrons, which are released thermally from the traps and excited into the conduction band, have a higher probability to be re-trapped by an electron trap than to recombine with a hole at a luminescence center, i.e. $A_N(n - N) >> A_m m$ or $A_N N >> A_N n$, $A_m m$. Since it is assumed in this section that charge transfer takes place only between one kind of trap and one kind of recombination center, we can write $m=n+n_c$. We take into account that conduction electrons are trapped very quickly, which means $n >> n_c$. This leads to

$$I = \frac{A_m}{A_N} v(T) \frac{n\, n}{N-n} = \frac{A_m}{A_n} \frac{s}{N} \exp\left(\frac{-E}{k_B T}\right) n^2\,. \tag{2.9}$$

During TL the temperature increases linearly with time, i.e.

$$\frac{dT}{dt} = \beta \quad \text{or} \quad T = T_0 + \beta t \,. \tag{2.10}$$

Here T_0 is the initial temperature at time t=0 and β is the heating rate. To find the time, or equivalently, the temperature dependence of the TL intensity and to construct the glow curve, which is represented by the light output as a function of the sample temperature (or the time), one needs to know the concentration of the filled electron traps as a function of the temperature during the TL experiments. Substituting (2.6) into (2.2) and using (2.10) we obtain

$$\frac{dn}{dt} = -\frac{v(T)}{\beta} n \frac{A_m m}{A_N (N-n) + A_m m} \,. \tag{2.11}$$

For the above-mentioned cases of *first-* and *second-order kinetics* (2.11) transforms into two closed equations

$$\frac{dn}{dT} = -\frac{v(T)}{\beta} n \qquad \textit{First-order kinetics} \tag{2.12}$$

and

$$\frac{dn}{dT} = -\frac{v(T)}{\beta} \frac{A_m}{A_N} \frac{n^2}{N-n} \approx -\frac{v(T)}{\beta} \frac{A_m}{A_N} \frac{n^2}{N} \,. \qquad \textit{Second-order kinetics} \tag{2.13}$$

Solutions of these equations together with (2.8) and (2.9) yield the temperature dependence of the TL intensity, which is peak-shaped and is called the glow curve.

We have simulated the TL experiment for particular *first-* and *second-order* cases. Figure 2.4 shows the concentration of filled electron traps and the concentration of free electrons in the conduction band during thermal excitation. In both cases the concentration of filled electron traps decreases with increasing temperature, whereas the concentration of free electrons increases to a maximum value at characteristic temperature; above this temperature it decreases. The decrease of the concentration of filled electron traps in first-order kinetics is faster than the decrease of the filled electron traps in second-order kinetics, because in the first-order case it is assumed that re-trapping is negligible. As a consequence, excitation of trapped electrons to the conduction band leads unavoidably to annihilation by recombination with trapped hole centers, whereas in the second-order process the trapped electrons might need two or more excitations in order to annihilate.

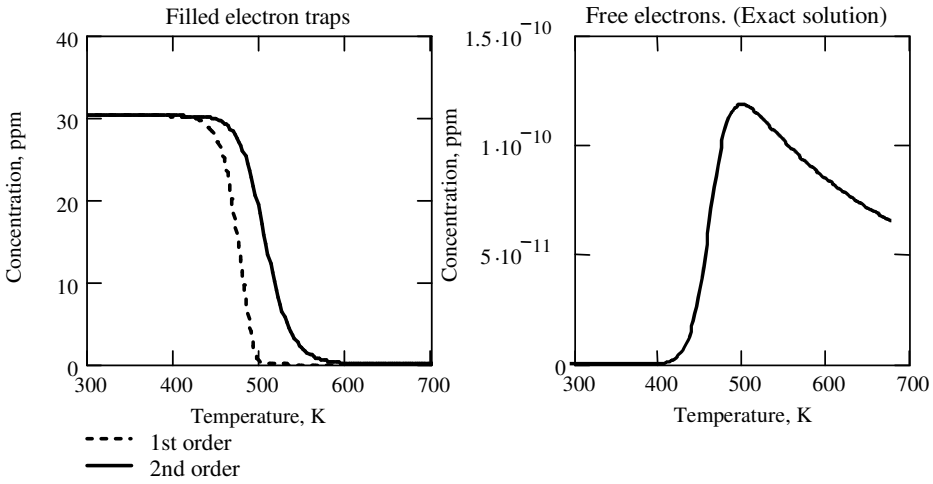

Figure 2.4. *Concentrations of filled electron traps for the first- and second-order approximation (left) and the exact solution of the differential equations for the concentration of free electrons in the conduction band (right) during the TL measurement.*

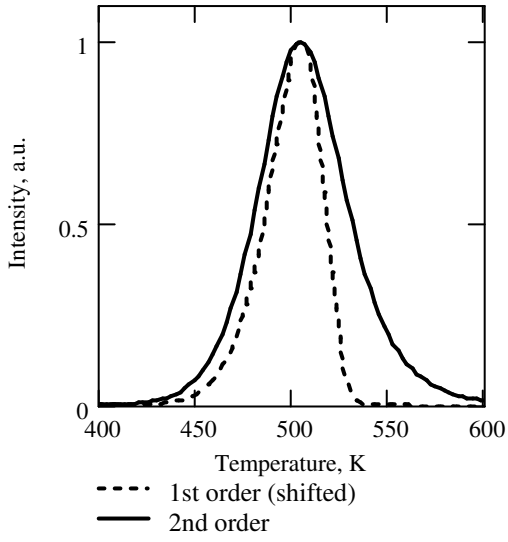

Figure 2.5. *Computed TL peaks for first-order (---) and second-order (—) kinetics. Both peaks are normalized to the corresponding maximum values; the first-order-kinetics peak is shifted slightly along the T-axis.*

The simulated *first-* and *second-order* glow curves are shown in figure 2.5. The basic difference between the *first-* and *second-order kinetics* is reflected in the symmetry of the TL peak. The characteristic feature of the first-order peak is that it is asymmetric. Above the temperature of the maximum TL the TL intensity decreases very rapidly with increasing T because in first order kinetics re-trapping does not play a role. The characteristic feature of the second order peak is that it is almost symmetric, because re-trapping slows down the process of annihilation.

The discussion of the model of Randall and Wilkins is based on the relatively simple situation in which, only one kind of trap and one kind of recombination center are active. The two examples discussed so far, *first-* and *second-order kinetics*, are only special cases. Even if the simplifying conditions are assumed to be true in general, the resulting equations consist of many intermediate cases that do not have a distinct order of kinetics.

In practice and in particular in natural minerals, several trapping and recombination sites exist giving rise to a multitude of peaks, which may or may not overlap. For a general description of the TL process, we need to take into account that the traps show a wide distribution of energy values. In addition we have to take into account several highly relevant processes, including trapping of charge carriers by recombination (luminescence) centers, trapping by non-radiative centers, mutual recombination, recombinations with defects of opposite charges at trapping centers, redistribution of electrons and holes over the available traps and luminescence centers (re-trapping) due to thermal excitation into the conduction and valence band. In chapter 7 a kinetic model of zircon TL is presented to improve our understanding of the processes involved in filling of electron and hole traps during radiation, fading, annealing and TL.

2.4 TL method

The development of thermoluminescence (TL) dating started in the late 1960s, initially for samples from pottery and other forms of baked clay. The TL, observed from these samples, is emitted by quartz, feldspar, zircon or a few other minerals. An early application was the determination of the age of art ceramics for museums and art auction rooms. During the 1970s advanced dating methods were developed for archaeological pottery (Sutton and Zimmerman, 1976), and an increasing understanding of the technical problems has been obtained. TL dating of baked clay products is possible because resetting is ensured by the fact that during the production of pottery the objects were heated to high temperature. More recently TL dating has been extended to sediment samples (Wintle and Huntley, 1980; Singhvi et al., 1982; Debenham, 1985; Smith, 1988; Van Es et al., 2000).

Thermoluminescence dating is based on the measurement of the number of light quanta emitted during heating by certain minerals, e.g. quartz, feldspar, flint, calcite and zircon. Luminescence originates from defect centers, which are created in the crystal lattice as a result of exposure to natural radioactivity. The total number of light quanta emitted by the sample is a measure for the dose to which the minerals were exposed since their deposition, and the time elapsed since burial. The crucial condition required for dating of sediments is

that exposure to sunlight causes the luminescence centers to be destroyed (optical bleaching). As a result, after the last exposure to sunlight the dating "clock" is started from time 0.

2.4.1 Equivalent dose

The equivalent dose (ED) is the laboratory irradiation dose that reproduces the natural TL signal. The latter signal is obtained after exposure of the mineral to ionizing radiation from natural radioactivity associated with impurities within the grains, radioactive nuclides in the immediate vicinity of the dating grains and cosmic irradiation. The sensitivity for TL differs from sample to sample. It depends on the efficiency of the processes leading to the formation of radiation damage centers, which in many cases depends strongly on the presence of impurities and other defects. It also depends on the optical quality of the mineral. There is no general rule relating the measured light intensity to the total received dose. This implies that the dose needed to reproduce the natural dose, the ED, has to be determined carefully by independent experiments.

In the literature, several methods have been designed to determine the equivalent dose. This is due to the fact that TL of natural samples is complex. To obtain information about the nature of natural TL, Wintle has examined for sediment samples the effect of sunlight and found that exposure to sunlight did not erase the natural TL signal completely (Wintle et al., 1979). Similar results were obtained in experiments with very long sunlamp exposures (> 1000 hours) and the remaining signal was called the residual TL. It is assumed that this residual TL signal is at least partly due to the presence of TL centers that cannot be bleached easily by light, and it may also include a component, which even does not originate from radiation induced defects. Therefore, it is assumed that, in some cases, the natural TL, I_{nat}, of a sediment sample consists of two components,

$$I_{nat} = I_0 + I_d \ . \tag{2.14}$$

Here I_0 is the residual TL, which is assumed to be the TL, already present at the time of deposition, and I_d is the TL due to the radiation dose since deposition.

Estimates of ED are obtained by comparing the natural TL with TL produced by calibrated laboratory doses. Theoretically this comparison can be translated into a function of time. In the methods, which have been developed to calculate the ED, it is assumed that the natural irradiation conditions can be accurately measured or calculated, and that the TL response is the same for natural or artificial irradiation. It is also assumed that any competition of electron-trap filling during natural or laboratory irradiation remains the same and that electron and hole traps are stable over the relevant periods of geological time. Some of these assumptions have been proven valid whereas others remain under investigation and have placed certain constraints on the methods (Wintle, 1997; Olley et al., 1998; Murray and Roberts, 1998; Murray and Wintle, 2000a and b).

We will discuss the advantages and disadvantages of the two methods in the ideal situation (i.e. without any residual TL), which are currently applied to determine the equivalent dose: (i) the regenerative dose method and (ii) the additive dose method.

2.4.1.1 The regenerative dose method

In the regenerative dose method the natural TL (NTL) of the sample is compared with the TL resulting from laboratory radiation (figure 2.6). The development of the natural TL signal starts after resetting, which is fundamentally different for pottery and sediments. It is well known that in pottery resetting has taken place by heating to high temperatures, while in sediments it takes place as a result of exposure to sunlight. This has led to differences in details of the protocols used to determine the equivalent dose, including the method of the regenerative dose. In pottery dating, the TL signal is obtained by irradiating the grains to a laboratory dose (D_i) after they have been heated, to release and measure the natural TL signal and annihilate the TL-producing centers. In sediment dating, the TL signal is regenerated by irradiating the grains, which have been optically bleached prior to irradiation. The sample is split into a number of portions because for each data point a new portion must be used. One portion is used to measure the natural TL. The remaining sub-samples are irradiated with various radiation doses (D_1-D_5) and the TL intensity of the samples is measured subsequently, thereby regenerating the thermoluminescence growth curve. Figure 2.6 shows the schematic representation of the regeneration method. The natural TL is known and when the natural dose is between D_1 and D_5, ED is obtained by interpolation (Wintle and Huntley, 1980).

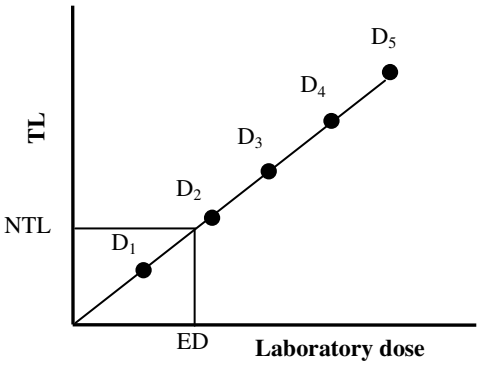

Figure 2.6. *Schematic representation of the regenerative dose method. Natural TL (NTL) is compared with TL of annealed samples after laboratory radiation. The ED is obtained by interpolation.*

An advantage of the regeneration method is that the ED is obtained by interpolation, which yields ED to a relatively high precision. A serious disadvantage of the regeneration method is that heating or bleaching might alter the sensitivity of the sample, implying that the regenerated TL growth does not accurately represent the growth of the TL signal during antiquity. In those cases one should apply proper corrections to interpret the TL results.

2.4.1.2 Additive dose method

In the additive dose method, measurements are made on a number of portions of the sediment sample. The natural TL signal is measured with the first portion. Each of the remaining portions is given a different additional laboratory dose (D_i). This results in an increase of the luminescence signal. In this method it assumed that the "dating clock" was set to zero at the time of deposition. ED is determined by the intersection of the straight line

obtained from the data points associated with the natural dose (ND), ND+D_1, ND+D_2, and ND+D_3 and the horizontal axis (figure 2.6) (Aitken, 1974).

The advantage of the additive dose method is that the sensitivity of the sample is not altered by any laboratory procedure to set the signal to zero, i.e. by heating or bleaching. The disadvantage of the additive dose method is that it involves extrapolation, which leads to increased statistical uncertainties in the determination of the age. From figure 2.6 it can be seen that the value of ED is obtained outside the experimental data set.

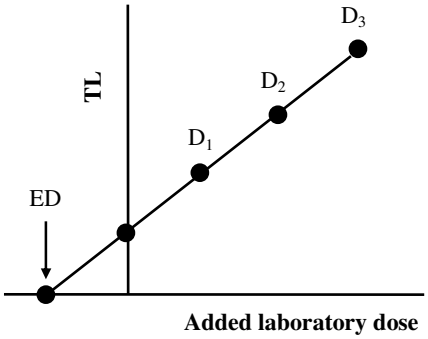

Figure 2.7. *Luminescence output as a function of the added dose. The Equivalent Dose (ED) is determined by the intersection of the straight line with the x-axis.*

It should be noted that for both the regeneration and the additive dose method linear growth of the TL intensity with the dose is not a necessary condition for dating but it is highly preferable. The growth of thermoluminescence with the dose is not always linear; in some cases one observes an initial supralinear range where the sensitivity increases with increasing dose, followed by a linear range characterized by constant sensitivity, as a function of the dose. Finally the sensitivity decreases due to the onset of saturation; the 'saturation' level is not necessarily the same for all samples of the same mineral. The range of supralinearity has been observed only for beta and gamma irradiation and not for alpha irradiation (Aitken, 1985).

The additive dose and the regeneration dose method are used in multiple-aliquot and single-aliquot protocols (see e.g. Murray and Roberts, 1998; Murray and Wintle, 2000a and b). In the multiple-aliquot protocol, the measurements are carried out on a multitude of sub-samples. For TL dating this is necessary because the TL measurement is destructive and the TL sensitivity of the sample is affected. In the single-aliquot protocol, multiple measurements are made on one portion of the sample. The practical advantage of this protocol is that only a small number of grains is needed to estimate the equivalent dose, whereas in the multiple-aliquot protocol large numbers of grains are required. Another practical advantage of the single-aliquot protocol is that subsequent steps, like preheating and TL measurements, can be performed readily with a sophisticated and automated reader.

Although there are some advantages to use the single-aliquot protocol, for dating procedures it is essential that prior to any measurement the sub-samples should be identical as much as possible. This means for example that any treatment of the sample that might change the sample's TL sensitivity must be avoided. The additive dose method with the multiple-aliquot protocol allows us to prepare sub-samples, which had been subjected - apart from the added dose- exactly the same pretreatment. Therefore we decided to use this method to determine ED.

2.4.2 Natural dose

Natural TL in zircon results from continuous exposure to nuclear radiation from uranium and thorium impurities within the sample itself, from uranium and thorium in distant grains, from potassium (present in e.g. K-feldspar) in the sedimentary environment and from cosmic radiation. (See chapters 3 and 8).

The basis of TL dating is the "age" equation:

$$Age\,(years) = \frac{ED\,[Gy]}{AD\,[Gy/a]}\,. \tag{2.15}$$

Here ED is the equivalent dose and AD is the dose to which the crystal is exposed annually. In zircon the build-up of the age-dependent luminescence is dominated by radioactive decay within the zircon grains due to the presence of trace amounts of uranium and thorium, which irradiate the material internally with α-particles. The range of the α-particles originating from U and Th is 10-40 μm, which is smaller than the zircon grain itself (70-100 μm). Therefore zircon TL is predominantly due to internal radiation and the corresponding dose rates are much higher than those from external sources in the sedimentary environment. The annual dose can be calculated from the activity concentrations of the relevant α-emitting nuclei in zircon, which have been determined with γ-ray spectrometry. The natural radionuclides providing the annual dose have very long half-lives and therefore the annual dose rate is assumed to be constant. For a more detailed and quantitative discussion of the dose rate response, the saturation dose, and the internal and external sources we refer to chapters 7 and 8.

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